

Structure of a Bicyclopropylidene Derivative. X-Ray Investigation of *trans*-2,2'-Bis(phenylthiomethyl)-1,1'-bicyclopropylidene

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In order to resolve the stereochemistry of a unique bi-cyclic system, the structure of the title compound was determined using X-ray diffraction techniques. Structural studies on this type of ring system have not been reported to date. The chemical synthesis and reactivity will be the subject of an article to be published.¹

Data for unit cell determination and intensity data were collected using a SYNTEX PI four-circle diffractometer with MoK α radiation ($\lambda = 0.71069$ Å). The temperature at the crystal site was kept at -150 °C and the specimen dimensions were $0.4 \times 0.4 \times 0.3$ mm. The $\theta/2\theta$ scan technique was employed with scan speed of $3-6$ ° min⁻¹ and a scan width of 2.2 °. A total of 2505 independent reflections with $\sin \theta/\lambda < 0.7$ Å⁻¹ were measured, of these 2434 were larger than $2.5\sigma(I)$ and were retained for structure analysis.

Crystal data. C₂₀H₂₀S₂, *trans*-2',3-bis(phenylthiomethyl)-1,1'-bicyclopropylidene, monoclinic: $a = 18.497(4)$ Å; $b = 5.644(1)$ Å; $c = 16.654(1)$ Å; $\beta = 108.39(1)$ °; $V = 1649.8$ Å³; ($t = -150$ °C); $M = 324.50$; $Z = 4$; $F(000) = 688$; $D_x = 1.306$ g cm⁻³. Space group C2/c (No. 15).

The structure was determined by direct methods. Full-matrix least squares refinement of all positional parameters and anisotropic thermal parameters for non-hydrogen atoms (the isotropic B -value for the hydrogen atoms was fixed at 2.0 Å²) converged to a conventional R value of 0.026, $R_w = 0.030$ and $S = 1.46$. In the final stages of the refinement only high-angle data ($\sin \theta/\lambda > 0.45$ Å⁻¹), were included in order to reduce the influence of bonding electrons on the positional parameters.

A description of the computer programs employed is given in Ref. 2. The atomic form factors used were those of Doyle and Turner³ for S and C, and of Stewart, Davidson and Simpson for H.⁴

The positional parameters are listed in Table 1. A tabulation of the thermal parameters and of the structure factors is available from the author.

Fig. 1 is an ORTEP drawing of the molecule, showing the atomic labelling. Pertinent structural parameters are listed in Table 2.

The space group demands the molecule to either possess a two-fold axis or a centre of symmetry.

Table 1. Fractional atomic coordinates. For numbering of atoms, see Fig. 1.

Atom	X	Y	Z
S	0.18250(1)	0.23351(4)	0.56346(1)
C1	0.02086(5)	0.54662(17)	0.47907(6)
C2	0.08782(5)	0.52296(19)	0.44965(6)
C3	0.03930(5)	0.75218(21)	0.43501(6)
C4	0.16610(5)	0.52558(17)	0.51511(6)
C5	0.27062(4)	0.26291(16)	0.64429(5)
C6	0.31950(5)	0.45722(17)	0.65282(6)
C7	0.38750(5)	0.46511(19)	0.72018(6)
C8	0.40766(5)	0.28061(21)	0.77847(6)
C9	0.35942(6)	0.08556(19)	0.76943(6)
C10	0.29093(5)	0.07678(17)	0.70288(6)
H31	0.0613	0.8912	0.4668
H32	0.0055	0.7820	0.3766
H2	0.0848	0.4239	0.3989
H41	0.2084	0.5575	0.4898
H42	0.1688	0.6506	0.5626
H6	0.3060	0.5896	0.6124
H7	0.4206	0.6009	0.7275
H8	0.4541	0.2899	0.8249
H9	0.3742	-0.0436	0.8099
H10	0.2562	-0.0530	0.6972

The latter symmetry turned out to be correct; the molecule is thus the *trans* isomer.

The geometry of the phenylthiomethyl moiety is normal. The two C-S bond lengths [C4-S of 1.818(1) Å and C5-S of 1.764(1) Å] are different because of the different hybridization states of the carbon atoms. The angles C4-S-C5 (103.7°) and S-C5-C6 (124.3°) are large because of repulsion between the hydrogen atoms on C4 and on C6. The side chain of the phenyl group; including C2, has the extended conformation, C6-C5-S-C4: 11.3(1)°, C5-S-C4-C2: 175.1(1)°.

Cyclopropane derivatives usually have structures and reactivities corresponding to that found in compounds with sp^2 hybridized carbon atoms. The bicyclopropylidene moiety of the present compound has a geometry which necessitates another description. The central C-C bond length, 1.303(1) Å is closer to that of a double bond between sp hybridized carbon atoms (*i.e.* 1.283 Å in the central

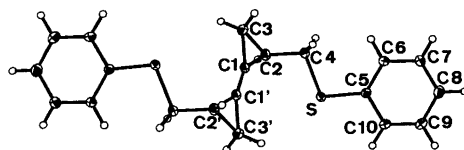


Fig. 1. ORTEP plot of the structure.

Table 2. Structural data. The numbering of the atoms is given in Fig. 1. The estimated standard deviations (in parantheses) were calculated from the variance-covariance matrix.

Distance	(Å)	Distance	(Å)
S—C4	1.818(1)	S—C5	1.764(1)
C1—C3	1.469(1)	C1—C2	1.475(1)
C1—C1'	1.303(2)	C2—C3	1.549(1)
C2—C4	1.513(1)	C5—C6	1.400(1)
C5—C10	1.402(1)	C6—C7	1.397(1)
C7—C8	1.392(2)	C8—C9	1.395(1)
C9—C10	1.396(2)		
Angle	(°)	Angle	(°)
S—C4—C2	107.36(7)	C4—S—C5	103.74(4)
S—C5—C6	124.25(7)	S—C5—C10	116.16(7)
C2—C1—C3	63.52(7)	C1—C3—C2	58.41(7)
C1—C2—C3	58.07(7)	C3—C1—C1'	148.87(13)
C1—C2—C4	118.22(9)	C2—C1—C1'	147.40(13)
C3—C2—C4	118.71(9)	C5—C6—C7	119.70(9)
C6—C5—C10	119.59(8)	C5—C10—C9	120.18(9)
C6—C7—C8	120.75(10)	C7—C8—C9	119.58(9)
C8—C9—C10	120.19(10)		

C—C bond in butatriene⁵) than to a $C(sp^2)-C(sp^2)$ double bond (1.336 Å). The C1—C2 and C1—C3 bond lengths, 1.475(1) Å and 1.469(1) Å, respectively, are shorter than the corresponding bonds in bicyclopentyl [1.501(3) Å].⁶ The difference between the two is probably due to the influence of the substituent on C2. The C2—C3 bond [1.549(1) Å] is much longer than that previously found for a cyclopropane ring bond, but is comparable in length to those observed in cyclobutane.

The bicyclopentylidene moiety is not quite planar in the crystal, the torsion angle C2—C1—C1'—C3 being 9°. A Newman diagram of the double bond is shown in Fig. 2.

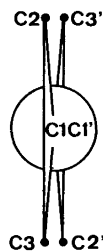


Fig. 2. Newman diagram of the central double bond.

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